Electronic Structure and Electron-Phonon Coupling in the 18K Superconductor Y_2C_3

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The electronic structure and electron-phonon coupling in Y_2C_3 is investigated using density functional calculations. We find that the Fermi level falls in a manifold of mixed character derived from Y d states and antibonding states associated with the C dimers in the structure. Calculations of the electron-phonon coupling for Y and C modes show that the former provide most of the coupling. Modes associated with C-C bond stretching have large matrix elements, but make small contributions to the coupling because of their high phonon frequencies. Substantial electron doping of the C-C antibonding states would yield a large increase in the coupling and critical temperature, perhaps to values comparable to MgB_2. However, it seems unlikely that a modification of Y_2C_3 with much higher filling of the C-C antibonding states can be stabilized.

The rare earth sesquicarbides, R_2C_3, where R is a rare earth or Y are a family of superconducting materials that form in the bcc Pu_2C_3 structure under high temperature conditions. Samples produced by arc melting have critical temperatures, T_c, of 10K to 12K, with little dependence on the particular rare earth. For example, as synthesized samples with the largest and smallest rare earths, specifically, La_2C_3 and Y_2C_3 have critical temperatures of 11K and 10.5K, respectively.[1–5] However, it was found early on that heavy Th doping raises T_c, up to 17K in the case of the Y compound.[6] Very recently, Amano and co-workers[7] reported that T_c for Y_2C_3 could be increased to 18K by synthesis under high pressure (4-5.5 GPa). The resulting samples have the same Pu_2C_3 structure as previously obtained samples but a slightly different lattice parameter, suggesting that the effect of pressure is to change the composition of the samples. Furthermore, they reported that the results were sensitive to the sintering conditions. The lattice parameters varied in the range a=8.181Å – 8.226Å, with reported T_c spanning the range 15K to 18K. The extrapolated upper critical field of the 18K samples was estimated to be $\sim$ 30T.[8]

The Pu_2C_3 structure has four formula units per primitive unit cell, spacegroup $I\bar{4}3d$, Y on site 16c (u,u,u) and C on site 24d $(v,0,1/4)$, where the coordinates are in terms of the bcc lattice vectors (see Fig. 1). As may be seen, C dimers with short bond lengths are a characteristic of this structure. Electronic structure studies of other metals with C dimers both at the tight binding[9] and density functional level[10] suggest that the electronic structure could have substantial C-C antibonding character near the Fermi level. Such states may be expected to have extremely high deformation potentials, reflecting these very strong C-C triple bonds. Also reflecting the very strong covalent bonds, phonons that modulate the C-C distances would be very stiff, which, if these states were responsible for the superconductivity, would yield a moderate electron-phonon coupling, λ, and a very high logarithmic average phonon frequency and therefore high

prefactor in the McMillan equation for T_c. In this scenario, a very strong dependence of T_c on stoichiometry (more precisely, occupation of the antibonding states) might be anticipated, as well as the possibility of very high T_c in more optimally doped samples, perhaps with values like in MgB_2 and A_3C_{60}. Here we report density functional calculations of the electronic structure and the coupling constants of a C-C and an Y mode aimed at determining the extent to which this scenario applies in Y_2C_3.

The present calculations were done using the general potential linearized augmented planewave (LAPW) method,[12] with local orbital extensions[13] to relax linearization errors and to treat the semi-core states of Y. LAPW sphere radii of 2.0 a_0 and 1.24 a_0 were used for Y and C, respectively. Well converged basis sets (convergence tests were done) consisting of 4250 basis functions for the 20 atom primitive cell were used, along with converged Brillouin zone samplings. The core states were treated relativistically and valence states semirelativistically. For the crystal structure we used the reported bcc $I\bar{4}3d$ Pu_2C_3 structure with the experimentally determined lattice parameter, $a = 8.226$ Å, from Ref. 7 but relaxed the internal coordinates using the calculated atomic forces. We found significant changes in the C-C dimer bond length from the available experimental refinement (Ref. 11). Specifically, we obtain a C-C distance of 1.33 Å, and a Y-C distance of 2.51 Å, corresponding to internal parameters, u=0.0504 and v=0.2940. The corresponding full symmetry Raman modes are an Y dominated mode at 175 cm^{-1} and an almost pure C-C bond stretching mode at 1442 cm^{-1}. It seems likely that the difference between our results and the C position of Ref. 11 is related to difficulty in the refinement due to sample stoichiometry, which is an issue in these sesquicarbides, as mentioned above.

The calculated electronic band structure and corresponding electronic density of states (DOS) are given in Figs. 2 and 3, respectively. The Fermi surfaces are displayed in Fig. 5. The band structure agrees qualitatively

with a very recent report by Shein and Ivanovskii,[14] although there are noticeable differences in detail, presumably related to the different C-C bond length in that calculation.

The band structure shows a manifold of 12 C $2s$ derived bands extending from -14.9 eV to -6.2 eV, relative to the Fermi energy, E_F (note that there are 12 C atoms in the primitive cell). This is followed by a narrower manifold of 18 C $2p$ bonding bands, associated with the C dimers. This, in turn, is separated by a ~ 2.5 eV gap from a broad manifold of mixed C-C antibonding and Y character. The Fermi level lies ~ 1 eV from the bottom of this manifold. Fig. 4 shows the contribution from states near E_F to the charge density. The plot is for the energy range that contributes 1 e per unit cell going down from E_F. This electronic structure is consistent with a conventional picture[9] of strongly covalently bonded C dimers embedded in a solid that has metallic cohesion involving mixture of Y and antibonding C-C states.

As may be seen, there are several bands crossing the E_F. This leads to a complex multisheet Fermi surface (Fig. 5), with no obvious strong nesting features.[15] The density of states at E_F is $N(E_F) = 1.88$ eV^{-1} on a per formula unit both spins basis, corresponding to a bare linear specific heat coefficient, $\gamma_{bare} = 4.4$ mJ/mol K^2. This is approximately 60% larger than the experimental value of $\gamma = 2.8$ mJ/mol K^2 (ref. 2), but this comparison should be interpreted with caution since the experimental stoichiometry was not well established. We note that Th doped Y$_2$C$_3$ with T_c=17K (closer to the 18K reported for Y$_2$C$_3$ by Amano and co-workers), has a reported experimental $\gamma = 4.7$ mJ/mol K^2, and that the DOS is peaked at the stoichiometric composition, implying that off-stoichiometric samples would likely have lower γ, both because of lower γ_{bare} and presumably lower electron phonon enhancement.

Considering the apparent absence of strong nesting, and the large unit cell (four formula units, 20 atoms), it is expected that the zone center modes may be at least semi-quantitatively representative for determining the electron-phonon coupling. As a further simplification, we focus on two modes in order to obtain the gross features. These are the two full symmetry modes related to the internal structural parameters. As mentioned, these are an Y dominated mode at 175 cm^{-1} and an almost pure C-C bond stretching mode at 1442 cm^{-1}. We determined the mode λ for these two modes using a frozen phonon method, in which LDA calculations were done as a function of the phonon distortion, and the deformation potentials calculated directly from the change in electronic structure on the Fermi surface. The result is shown as a function of rigid band Fermi energy in Fig. 6. For this plot, it was assumed that the lower frequency Y mode (which modulates both Y distances and Y-C distances) is representative of all modes except the 6 C-C bond stretching modes, which were assumed to be represented by the high frequency C-C mode. Most likely, this is reasonably good for the bond stretching modes but un-

derestimates the phonon frequency for the other modes, since the C dimers are lighter than an Y atom. However, considering the crudeness of representing the system with two full symmetry zone center modes, it hardly seems justified to attempt corrections, and instead we view the result as semi-quantitative.

The calculated electron-phonon coupling for the stoichiometric band filling is $\lambda = 0.6$ and is dominated by phonons other than the C-C bond stretching; the C-C bond stretching provides less than 10% of the total λ. Inserting $\lambda = 0.6$ into the McMillan formula, with μ^*=0.1 and ω=175 cm^{-1}, we obtain T_c=5K, which is fair agreement considering the crudeness of the approximation employed.

What is significant is that λ has a maximum at the stoichiometric band filling. This is related to the fact that the Fermi energy falls on a peak in the DOS. The dependence of λ on band filling and the difficult synthesis of stoichiometric sesquicarbides provides an explanation for the experimentally observed variability of T_c depending on preparation conditions. Going to lower band filling, λ decreases and then increases again to a value exceeding $\lambda = 1$, reflecting the structure of the DOS, but this only happens quite far down, corresponding to an electron deficiency of about 1 e per formula unit. The C-C strectching contribution is small throughout this region. Going to higher electron count, λ again decreases initially and then increases, again to values exceeding $\lambda = 1$. However, in this case the C-C bond stretching contribution becomes significant and as a result the logarithmic average phonon frequency also sharply increases. In principle, this would mean that heavily electron doped Y$_2$C$_3$ would become a high temperature superconductor, like MgB$_2$ and A_3C$_{60}$. However, this is based on a rigid band filling, which is a highly unlikely scenario. Instead, population of C-C antibonding states should be highly disfavored, and therefore it would be rather difficult to chemically reach the region where this contribution to λ becomes large.

In summary, we report electronic structure and mode electron-phonon calculations for Y$_2$C$_3$. The results are consistent with conventional electron-phonon mediated superconductivity related to Y - C phonons. The results show that the superconductivity is qualitatively like in other metal carbide superconductors, and not like MgB$_2$ or A_3C$_{60}$.

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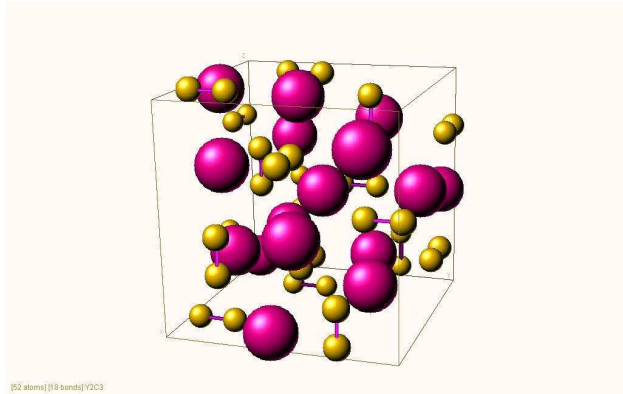[15] The middle jack shaped section could have some nesting between the flat parts along [111].
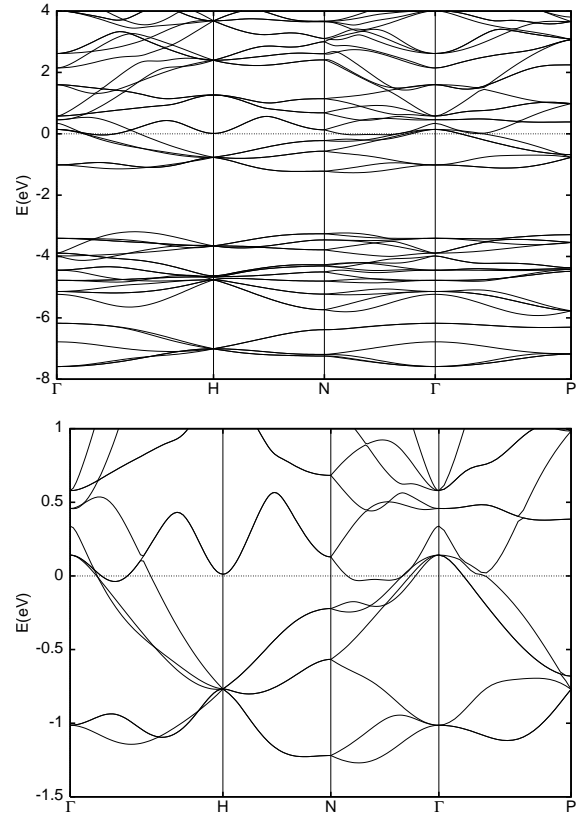
FIG. 2. Calculated band structure of Y_2C_3 with the relaxed atomic positions. The lowest bands shown are part of the C $2s$ manifold. The bottom of this manifold is at -14.9 eV. The lower panel is a blow-up around E_F, which is at 0 eV.
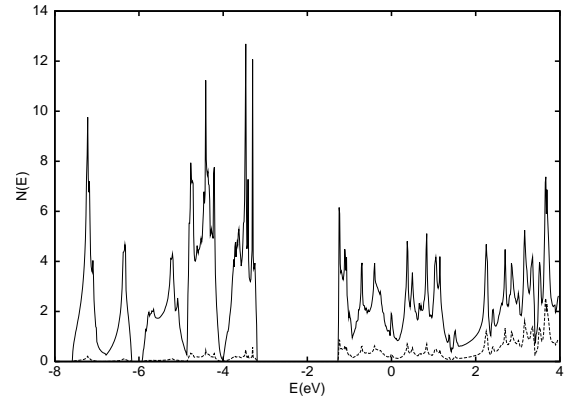

FIG. 3. Electronic density of states of Y_2C_3 with the relaxed atomic positions. The solid line is the total density of states on a per formula unit basis and the dashed line is the Y d contribution as defined by projection onto the Y LAPW sphere of radius 2.0 a_0.

FIG. 1. Crystal structure of Y_2C_3 showing the C_2 dimers. Large spheres denote Y and small spheres denote C.
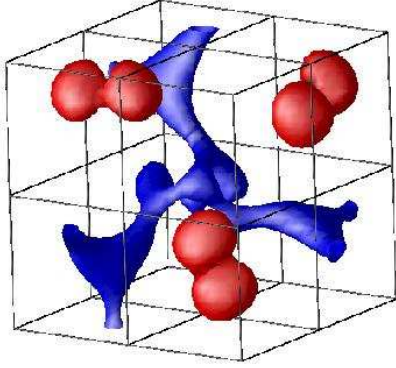
FIG. 4. This figure shows the charge density originating from the valence bands near E_F (see text) in 1/4 of the primitive unit cell around C (dumbells, red online) and Y (interconnected network, blue online). Isodensity surfaces correspond to $\rho(\mathbf{r})$ =0.00112 e/a_0^3 for C and 0.00092 e/a_0^3 for Y. Small differences between the charge density values were needed to improve visibility of the two surfaces. For the same puprose, the parts of the Y charge density surfaces, penetrating from the neighboring unit cells, were removed. Note the metallic like Y derived density and the C antibonding density.
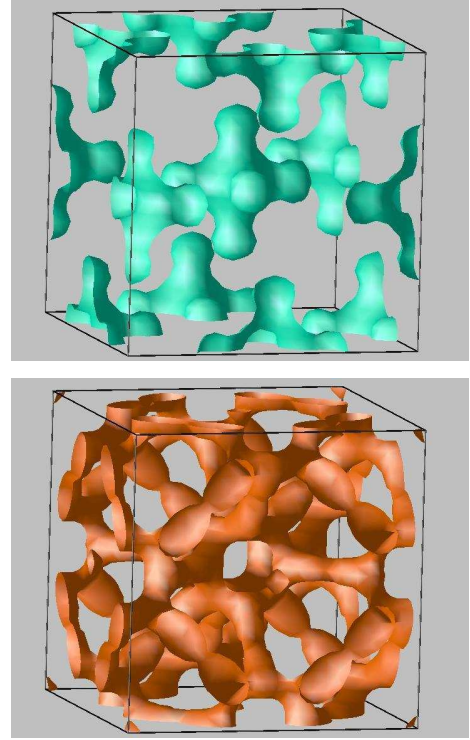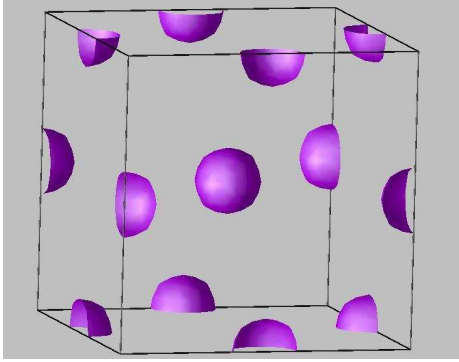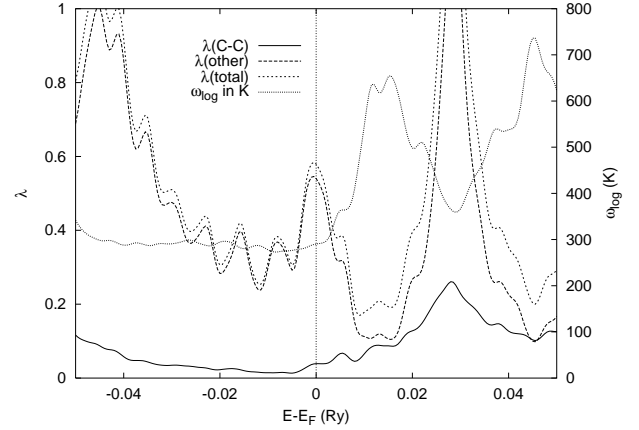
FIG. 5. LDA Fermi surfaces of Y_2C_3.

FIG. 6. Mode λ and average phonon frequency (see text) as a function of energy. The heavy dashed (heavy solid) line denotes the full symmetry Y (C) derived mode λ as a function of energy, normalized as if these modes are representative. The light dashed line is the total λ with this assumption. The light dotted line is the logarithmic average of these two frequencies with λ, which would enter the prefactor of the McMillan equation.